

Effects of Charge Carriers' Interactions on Seebeck Coefficients

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5.1 Introduction

The Seebeck effect is the development of an electromotive force (EMF) across a material in response to the imposition of a temperature differential. The ratio of the EMF to the temperature difference is defined as the Seebeck coefficient, α .

The Seebeck coefficient is a fundamental electronic transport property. In particular, the Seebeck coefficient measures the entropy transported with a charge carrier as it moves, divided by the carrier's charge. As such, the Seebeck coefficient is affected by charge carriers' interactions with one another, with phonons and with the local magnetic moments of magnetic solids. Information about these interactions is obtained by investigating how Seebeck coefficients vary with carrier density, temperature, and magnetic field.

The Seebeck effect is also of practical importance. Thermoelectric power generation results from imposing a temperature gradient across a material. Thermoelectric generators are used to convert thermal energy into electrical energy in remote locations, such as in rural areas and on rockets where connection to a central power grid is not possible. Seebeck coefficients are also central to Peltier cooling. Cooling occurs by the absorption of heat as an electrical current passes through a junction between materials with different Seebeck coefficients. Peltier refrigeration is widely used to cool electronic components.

The product of a material's thermoelectric figure-of-merit, Z , and the absolute temperature, T , assesses the material's value in both types of thermoelectric devices. In terms of fundamental transport coefficients, $ZT \equiv (\sigma T/\lambda)\alpha^2$; σ is the material's electrical conductivity, λ is its thermal conductivity, and

α is its Seebeck coefficient. Therefore, a material's Seebeck coefficient is crucial to its utility. ZT only depends upon the Seebeck coefficient if the material is a conductor that satisfies the Wiedermann–Franz relation, $\sigma T/\lambda = (3/\pi^2)(q/k)^2$, where q is the carrier's charge and k is the Boltzmann constant. Then $ZT \equiv (3/\pi^2)(q\alpha/k)^2$.

This article addresses how the Seebeck coefficient is affected by carriers' interactions with one another, with phonons, and with local magnetic moments. Distinctive contributions to the Seebeck coefficients can result from these interactions. As a result, the Seebeck effect is a very useful probe of these interactions. In addition, large augmentations of the Seebeck coefficients produced by carriers' interactions can greatly improve a material's utility in thermoelectric devices. In particular, high- and low-temperature enhancements of Seebeck coefficients can be exploited to facilitate high-temperature thermoelectric power generation and low-temperature Peltier cooling, respectively. This chapter will only present a few simple examples to illustrate some of the primary effects of carriers' interactions.

5.2 The Seebeck Coefficient

The Seebeck coefficient is the entropy transported with a charge carrier divided by the carrier's charge. It is useful to divide transported entropy into two components. The first component is the change of the net entropy of a solid attendant upon the addition of a charge carrier. The second component is the energy transported in the transfer process divided by the absolute temperature. Thus, the Seebeck coefficient is the sum of contributions associated with the presence of charge carriers and their motion:

$$\alpha = \alpha_{\text{presence}} + \alpha_{\text{transport}} \quad (5.1)$$

5.3 Noninteracting Charge Carriers

Simple treatments of the Seebeck coefficient restrict their attention to the first contribution, α_{presence} . In the absence of interactions, the solitary contribution to this term is just the change of entropy-of-mixing associated with adding a single charge carrier. For example, consider the idealized situation in which n fermion charge carriers are distributed among N degenerate states of an arbitrarily narrow energy band. Then the entropy of distributing n fermion charge carriers among the N states is

$$S = -Nk[c \ln c + (1 - c)\ln(1 - c)] \quad (5.2)$$

where $c \equiv n/N$ is the carrier concentration. The Seebeck coefficient is then related to the change of this entropy-of-mixing upon adding a single carrier:

$$q\alpha = \partial S/\partial n = k \ln[(1 - c)/c] \quad (5.3)$$

An alternative form of this simple expression is obtained when the carrier concentration is expressed in terms of the energy of the electronic energy band, the chemical potential, μ , and the thermal energy, kT , via the Fermi function, $c = 1/\{\exp[(E - \mu)/kT] + 1\}$:

$$\alpha = (k/q)[(E - \mu)/kT] \quad (5.4)$$

5.4 Electron–Electron Interactions

The preceding discussion of the Seebeck coefficient of noninteracting carriers has not explicitly considered charge carrier's spin. However, each electron carries a magnetic moment. Thus, each electronic orbital state can be occupied both by a carrier of spin up and by a carrier with spin down.

In the absence of interactions between carriers, the presence of carrier spin simply doubles the number of states available to a carrier. Then, with c denoting the number of carriers per orbital state, spin

degeneracy converts the Seebeck coefficient in the narrow-band limit from Equation 5.3 to¹

$$\alpha = (k/q)\ln[(2 - c)/c] \quad (5.5)$$

However, the Coulomb repulsion between carriers may preclude two carriers occupying the same site. Nonetheless, in this instance a carrier that occupies a site can equivalently have one of two spin values, spin up or spin down. The Seebeck coefficient is then¹

$$\alpha = (k/q)\ln[2(1 - c)/c] \quad (5.6)$$

This simple example indicates that electron-correlation effects, Coulomb repulsion between carriers, significantly affects the Seebeck coefficient.

5.5 Electron–Phonon Interactions

The electron–phonon interactions simply refer to the dependence of the electronic energy levels on the positions of a solid's atoms.² Thus, a solid's electronic states are altered as a solid undergoes thermal expansion. Furthermore, the relaxation of electronic carriers in response to atoms' relatively slow motions alters the frequencies of the associated atomic vibrations. Finally, a charge carrier that moves slowly enough can become self-trapped in the potential well produced by surrounding atomic displacements. These effects all manifest themselves in carriers' Seebeck coefficients.

5.5.1 Temperature-Dependent Shifts of Electronic Energy Levels

Changing temperature produces significant shifts of a semiconductor's electronic energy levels. There are two reasons for these shifts. First, a solid's thermal expansion alters the equilibrium positions of a solid's atoms. Second, the electron–lattice interaction causes altering of the amplitudes of a solid's atomic vibrations to change the energies of its charge carriers. Both of these effects shift the energy of a carrier from its value at absolute zero, E , by an amount that is proportional to the net energy of atomic vibrations

$$E_{\text{vib}} = \sum_{q=1}^N \hbar \omega_q (N_q + 1/2) \quad (5.7)$$

where N is the total number of phonon modes. Here, N_q and ω_q respectively denote the number and frequency of phonons of wavevector q . Thus the energy of the shifted state is

$$\varepsilon = E - (\gamma/kN) \sum_{q=1}^N \hbar \omega_q (N_q + 1/2) \quad (5.8)$$

In the high-temperature regime where $N_q \rightarrow kT/\hbar \omega_q$, the electronic energy shifts linearly with temperature: $\varepsilon = E - \gamma T$. The magnitude of the interaction parameter, γ , for states near the edge of a semiconductor's band is typically $10^{-4} - 10^{-3}$ eV/K. These shifts of the edges of a semiconductor's valence and conduction bands produce the commonly observed thermally induced shrinking of semiconductors' optical gaps.

The contribution to the Seebeck effect associated with the presence of a carrier of energy ε , $\alpha = \alpha_{\text{presence}}$, is³

$$\alpha(E) = \frac{(\langle \varepsilon + E_{\text{vib}} \rangle - \langle E_{\text{vib}} \rangle) - \mu}{qT} \quad (5.9)$$

where the energy associated with the addition of a charge carrier, the expression within curved brackets, is the difference between the thermally averaged energy of the system comprising thermal atomic

vibrations with and without the carrier's presence. Upon performing the thermal averages:

$$\alpha(E) = \frac{\left[E + \sum_{q=1}^N \left(\frac{\hbar\Omega_q}{2} + \frac{\hbar\Omega_q}{e^{\hbar\Omega_q/kT} - 1} - \frac{\hbar\omega_q}{2} - \frac{\hbar\omega_q}{e^{\hbar\omega_q/kT} - 1} \right) - \mu \right]}{qT} \quad (5.10)$$

where $\Omega_q \equiv \omega_q(1 - \gamma/kN)$. In the high-temperature regime, where the electronic energy level shifts linearly with temperature, the Seebeck coefficient becomes

$$\alpha(E) = \frac{[E - \mu]}{qT} \quad (5.11)$$

In this case, interactions that shift the energies of electronic states, as observed in optical measurements, do not affect the Seebeck coefficient. The shift of the electronic energy of a carrier is offset by the change in the net energy of the atomic vibrations to which the carriers are coupled.

5.5.2 Phonon-Drag: Low-Temperature Enhancement of the Seebeck Coefficient

“Phonon-drag” is a contribution to the Seebeck coefficient that is associated with the mechanism of carriers' transport, $\alpha_{\text{transport}}$. In particular, phonon-drag occurs when the momentum that is imparted to sound waves by itinerant electronic carriers is not readily dissipated.⁴ Then entropy flow continues after a carrier is scattered by sound waves. Phonon-drag can produce a large peaked low-temperature enhancement of the Seebeck coefficient. Phonon-drag augmentations of the Seebeck coefficient of about 4000 $\mu\text{V/K}$ at 50 K are found for high-quality silicon, germanium and diamond crystals with dopant density of less than 10^{17} cm^{-3} . However, phonon-drag contributions to the Seebeck coefficients of metals are much smaller.

As the temperature is lowered, the phonon-drag contribution to the Seebeck coefficient emerges as mechanisms that readily dissipate momentum imparted to sound waves are frozen out. The net momentum imparted to sound waves by a carrier is $p = qEf\tau$. Here, q is the carrier's charge, F is the electric field strength, f is the fraction of a carrier's momentum that is transferred to sound waves, and τ is the relaxation time for the dissipation of sound waves' momentum through their interactions with atoms. Specifically, sound waves disperse their momentum through interactions with high-energy phonons, point defects, and the sample's boundaries.

The entropy flow per carrier associated with the sound waves' net momentum is ps^2/T , where s is the sound velocity. The charge flow per carrier is $q\mu F$, where μ is a carrier's mobility. The ratio of these entropy and particle flows is the phonon-drag contribution to the Seebeck coefficient:

$$\alpha_{\text{transport}} = \left(\frac{ps^2/T}{q\mu F} \right) = \left(\frac{s^2\tau}{\mu T} \right) f = \frac{k}{q} \left(\frac{s^2\tau}{D} \right) f \quad (5.12)$$

where the mobility is expressed in terms of carriers' diffusion constant, D , via the Einstein relation, $\mu = qD/kT$. Both τ and $\alpha_{\text{transport}}$ of Equation 5.12 increase with decreasing temperature.

With decreasing temperature, τ ultimately becomes so large that the momenta of sound waves are dissipated primarily through their interaction with charge carriers. Then Equation 5.12 loses validity and the phonon-drag contribution to the Seebeck coefficient then becomes

$$\alpha_{\text{transport}} = \frac{k}{q} \left[\frac{N(T)}{n} \right] \quad (5.13)$$

where $N(T)$ is the density of acoustic phonons that interact strongly with charge carriers whose density is n . Since phonons and carriers interact most strongly when they have comparable wavelengths, the density of phonon states, with which carriers interact, essentially equals the density of thermally

accessible carrier states. These densities and $\alpha_{\text{transport}}$ fall to zero as the temperature is decreased. Thus, when dissipation of sound waves momenta by interactions with phonons and with carriers are both considered, phonon-drag produces a contribution to the Seebeck coefficient that is a peaked function of temperature.

5.5.3 Phonon-Assisted Hopping

In conventional semiconductors an electronic charge carrier moves between atomic sites too rapidly for surrounding (relatively slow moving) atoms to alter their positions in response. However, when electronic motion is slowed sufficiently, a charge carrier can “collapse” into a “self-trapped state.” Then the electronic carrier is bound within the potential well that is produced as surrounding atoms assume altered equilibrium positions. The unit comprised of the self-trapped charge carrier and the pattern of atoms with displaced equilibrium positions is termed a “polaron.”

Polaron formation frequently occurs in ionic (i.e., polar) materials since the exceptional strength and long-range of their electron–lattice interactions render them especially effective. The imposition of disorder also often slows carrier motion enough to trigger polaron formation even in covalent solids.

A self-trapped charge carrier moves very slowly as it responds to the changing potential well associated with movement of the surrounding atoms. If the change of the strain energy associated with moving a carrier between adjacent sites exceeds the electronic transfer energy, motion of the self-trapped carrier becomes incoherent. Polaron motion is then described as occurring by a succession of thermally assisted hops.

The contribution to the Seebeck coefficient associated with polarons' presence is¹

$$\alpha_{\text{presence}} = \frac{k}{q} \left(\frac{E_p - \mu}{kT} \right) \quad (5.14)$$

where E_p is the energy of the polaron, the electronic energy of the self-trapped carrier plus the strain energy required to produce the associated atomic displacements. When hopping occurs between inequivalent sites of a disordered material¹:

$$\alpha_{\text{presence}} = \frac{k}{q} \left(\frac{\langle E_p \rangle - \mu}{kT} \right) \quad (5.15)$$

where $\langle E_p \rangle$ is the average polaron energy at the sites involved in the transport. The Seebeck coefficient is augmented by the average energy transferred with a carrier as it hops¹:

$$\alpha_{\text{transport}} = \frac{1}{qT} \left\langle (E_f - E_i) \frac{(\Gamma_i - \Gamma_f)}{(\Gamma_i + \Gamma_f)} \right\rangle \quad (5.16)$$

where E_i and E_f are the energies and Γ_i and Γ_f are the effective electron–lattice coupling strengths at the initial and final sites of a hop, respectively. This result indicates that inequivalence of both energies and coupling strengths are required for energy to be transported with a hopping carrier. However, the energies and the coupling strengths are related to one another: the effective electron–lattice coupling strength increases with the strength of a carrier's binding. As a result, energy is generally transported with a hopping carrier. Thus, $\alpha_{\text{transport}}$ usually contributes meaningfully to $\alpha = \alpha_{\text{presence}} + \alpha_{\text{transport}}$.

5.5.4 Carrier-Induced Softening

Charge carriers in molecular solids often can move more rapidly about a molecule than they can move between molecules. A carrier can then readily adjust to displacements of the atoms with which it interacts. This relaxation of a carrier lowers the energetic cost of the associated atomic displacements.

Thus, the accommodation of a carrier to atomic motions lowers the associated vibration frequencies, thereby increasing atoms' vibratory entropy.⁵

Such carrier-induced softening augments α_{presence} . In particular, a carrier is associated with enhanced vibratory entropy that travels along with a carrier's intermolecular motion. This contribution rises as the temperature is increased from absolute zero until a plateau is reached when the thermal energy, kT , exceeds the associated vibration energies.

Carrier induced softening also contributes to $\alpha_{\text{transport}}$ for hopping carriers. In particular, the softening of an occupied molecule facilitates its deformation relative to that of an unoccupied molecule. As a result, the deformation energy associated with a hop, the hopping activation energy, tends to be exchanged at occupied sites and thus transported with the carrier. This contribution to $\alpha_{\text{transport}}$ rises from absolute zero to a peak that occurs when kT is a significant fraction, $1/3$, of the vibration energy and then falls as temperature is increased further as $1/kT$. Distinctively, neither carrier-induced softening nor its contributions to the Seebeck coefficient depend on the carrier density.

Molecules with high orbital electronic degeneracy are especially polarizable.⁶ This effect may account for the large contribution from carrier-induced softening ($\approx 300 \mu\text{V/K}$ at 300 K) found in boron carbides, where carriers hop between 12-atom icosahedral units.^{7,8}

5.6 Magnetic Interactions

Paramagnetic semiconductors contain ions with local magnetic moments. Charge carriers interact with these moments via two types of exchange interaction. Carriers that occupy a magnetic ion interact with the local moments of that ion via intrasite exchange, I . Meanwhile, a carrier interacts with the spins of other sites by intersite exchange.

Intrasite exchange is typically so strong, $I \gg kT$, that it dictates how the carrier will align with the occupied site's spins. Strong intrasite exchange ensures that the addition of a carrier of spin $1/2$ changes the net spin of a magnetic ion from S to $S \pm 1/2$. Since an isolated paramagnetic ion can assume $2S + 1$ equivalent orientations, a carrier's presence changes the site's spin entropy by $k \ln[(2S + 1 \pm 1)/(2S + 1)]$. The larger the spin of the magnetic ion, the smaller the effect on the spin-orientation entropy of adding a carrier. Adding a carrier to a nonmagnetic site, $S = 0$, produces the maximum spin entropy, $k \ln(2)$, as described in Section 5.4.

The effect of intersite exchange on the spin entropy associated with a charge carrier is opposite that from intrasite exchange. For example, increasing a site's spin through the addition of a carrier enhances the exchange forces between the occupied site and neighboring magnetic sites. This carrier-related increase of the intersite exchange forces tends to reduce the spin-orientation entropy of surrounding sites. Thus, the spin contribution to the Seebeck coefficient associated with a carrier's presence has the form⁹

$$\alpha_{\text{presence}} = \frac{k}{q} \left[\ln \left(\frac{2S + 1 \pm 1}{2S + 1} \right) \mp A \left(\frac{T_0}{T} \right)^2 \right] \quad (5.17)$$

where T_0 is the magnetic ordering temperature and A is a numerical constant.

5.7 Summary

Charge carriers' interactions with one another, with phonons, and with the localized magnetic moments of a magnetic semiconductor substantially affect the Seebeck coefficient. Understanding these effects is essential to interpreting Seebeck effect measurements. Furthermore, carriers' interactions can enhance the Seebeck coefficient and thereby significantly improve high-temperature thermoelectric power generation and low-temperature Peltier cooling.

Interactions between charge carriers impose restrictions on the states they can occupy, thereby decreasing their Seebeck coefficient. However, interactions between carriers and the localized electrons of a paramagnetic solid can significantly augment the Seebeck coefficient.

Thermally induced shifts of the valence and conduction band states affect the Seebeck coefficient of a conventional semiconductor only modestly. The underlying interaction shifts atoms' vibration frequencies as well as electronic energy levels. Taken together these two shifts produce nearly compensating effects on a semiconductor's Seebeck coefficient.

Phonon-drag can produce a large low-temperature enhancement of the Seebeck coefficient. Phonon-drag occurs when momentum that is transferred from charge carriers to sound waves is not readily dissipated. As temperature is lowered, the Seebeck coefficient rises as scattering of sound waves by phonons diminishes. Ultimately, sound waves are predominantly scattered by the carriers themselves. The phonon-drag contribution then falls with decreasing temperature.

Seebeck coefficients of carriers that hop between localized states depend strongly on electron–lattice interactions. Through its electron–lattice interaction, a localized carrier affects surrounding atoms in two ways. A localized carrier induces shifts of the equilibrium positions of surrounding atoms. In addition, alteration of a localized carrier's wave function, in response to atomic motions, shifts their vibration frequencies. Carrier-induced shifts of atoms' equilibrium positions affect the Seebeck coefficient. The Seebeck coefficient is also affected by the atomic-vibration energy that is generally transferred with charge carriers that hop between inequivalent sites. In addition, large polarizable localized electronic states induce significant softening of the atomic vibrations to which they are coupled. Transport of the enhanced vibration entropy associated with softened vibrations contributes to the Seebeck coefficient. In addition, vibration energy is carried with a carrier as it jumps from softened sites.

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